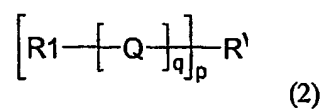
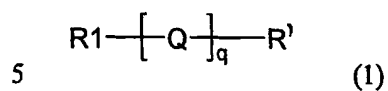


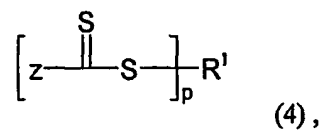
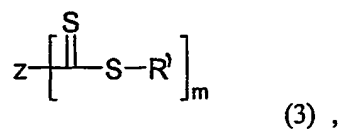
Claims

1. A method of making a functionalised polymer of Formula (1) or Formula (2).



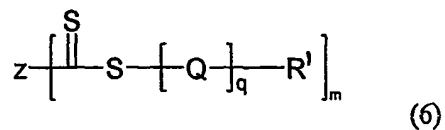
comprising the steps of:

- 10 reacting a thiocarbonyl thio compound of Formula (3) or Formula (4);

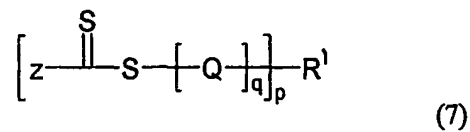


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an olefinically unsaturated monomer (Q), and a first source of free radical to form a Polymer of Formula (6) or Formula (7);



20



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and subsequently contacting the polymer of Formula (6) or Formula (7) with a second source of free radicals, the second source of free radicals comprising a radically transferable functional moiety R1, to form a polymer of Formula (1) or Formula (2) and a compound of Formula (3) or Formula (4);

5

wherein:

R1 is moiety comprising a functional group;

10 R' is selected from the group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups;

15 Z is selected from (i) a solid support, (ii) Z comprises a linker attached to a solid support, and (iii) Z is a group selected from a straight or branched chain, substituted or non substituted C₁ to C₂₀ alkyl (especially a C₁ to C₄ alkyl such as methyl or ethyl); optionally substituted aryl, e.g. phenyl, substituted phenyl; phenyl covalently bonded to a polymer; optionally substituted heterocyclyl, substituted or non-substituted C₁ to C₂₀
 20 (especially C₁ to C₄) alkoxy, optionally substituted alkyl thio, thioalkoxyl (optionally substituted with a polymer); substituted or non-substituted benzyl (optionally substituted with a solid support), optionally substituted aryl oxycarbonyl (-COOR''), carboxy (-COOH), optionally substituted oxyloxy (-O₂CR''), optionally substituted acyloxy (-CO₂CR''), optionally substituted carbonyl (-CONR''₂), cyano (-CN), dialkyl- or diaryl
 25 phosphonato (-P(=OR''Z), dialkyl- or diaryl-phosphinato [-P(=O)R''Z] or SCH₂CH₂CO₂T (where T is a solid support or a polymer); the linker may optionally comprise a straight or branched chain, substituted or non substituted C₁ to C₂₀ alkyl (especially a C₁ to C₄ alkyl such as methyl or ethyl); phenyl, substituted phenyl; phenyl covalently
 30 banded to a polymer; substituted or non-substituted C₁ to C₂₀ (especially C₁ to C₄) alkoxy, thioalkoxyl (optionally substituted with a polymer); substituted or non-substituted benzyl;

most preferably Z is a solid support or a linker attached to a solid support;

55

R" is selected from the group consisting of optionally substituted C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxyl, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

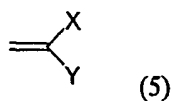
Q is at least one olefinically unsaturated monomer, optionally two or more different olefinically unsaturated monomers;

q = an integer of at least 2;

p = an integer of at least 1;

m = an integer of at least 1.

2. A method of making a functionalised polymer according to Claim 1, wherein the olefinically unsaturated monomer comprises vinyl monomers of Formula (5):

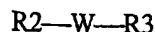


wherein X is selected from the group consisting of: hydrogen, halogen and substituted or unsubstituted C₁-C₄ alkyl, said alkyl substituents being independently selected for the group consisting of hydroxyl, alkoxy, OR", CO₂H, CO₂R", O₂CR" and combinations thereof; and

wherein Y is selected from the group consisting of hydrogen, R", CO₂H, CO₂R", COR", CN, CONH₂, CONHR", CONR"₂, O₂CR", OR" and halogen.

3. A method as claimed in claim 1 or claim 2 wherein the compound of Formula (3) or (4) is recovered at the end of the process.

4. A method as claimed in any preceding claim wherein the second source of radicals is a compound capable of forming a carbon or oxygen centred radical of Formula (8)



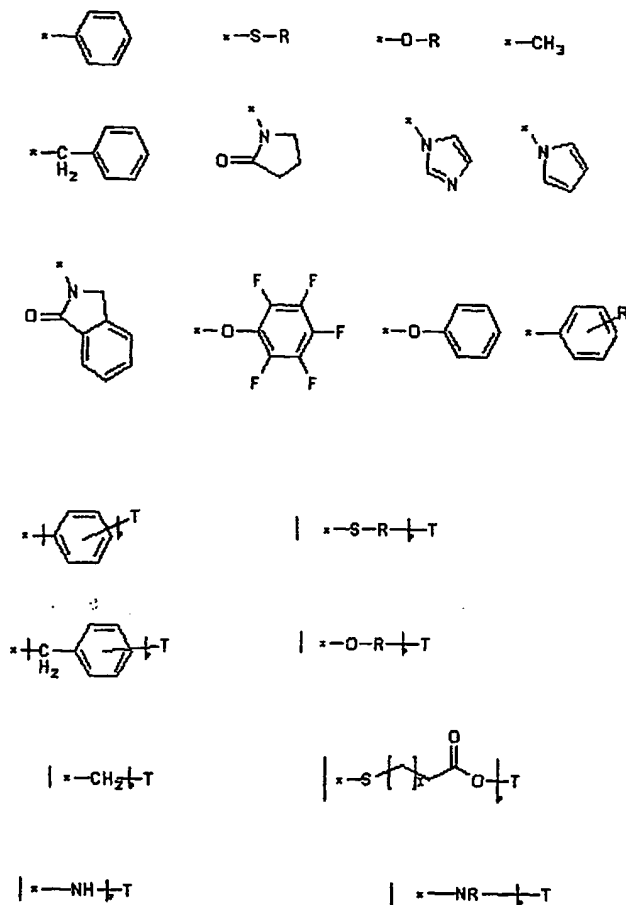
Wherein R2 and R3 are independently selected from the group R'; and W is a N=N bond, an O-O bond or a group that decomposes thermally or photolytically to form two residues containing a carbon or oxygen centred radical and at least one of R2 or R3 reacts with the polymer of Formula (6) or Formula (7) to leave the moiety R1 comprising the functional group.

5. A method according to claim 4, wherein R1, R2 and/or R3 may be the same or different and are selected from a group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups.

15

6. A method as claimed in any preceding claim wherein the group Z is selected from the group consisting of: methyl, ethyl, other C₁-C₄ alkyl, methylene covalently bonded to a polymer, methylene covalently bonded to a solid support T, phenyl, substituted phenyl, phenyl covalently bonded to a polymer, phenyl covalently bonded to solid support T, alkoxy, substituted alkoxy, thioalkoxy, substituted with a solid support T, benzyl, substituted benzyl, benzyl substituted with a polymer, benzyl substituted with a solid support T, SCH₂.CH₂.CO₂T wherein T is a polymer or solid support and preferably SCH₂.CH₂.CO₂T wherein T is a solid support or polymer.

7. A method as claimed in claim 6 wherein the group Z is selected from the group consisting of:



wherein T is a solid support selected from an organic compound, an inorganic compound or magnetised beads;

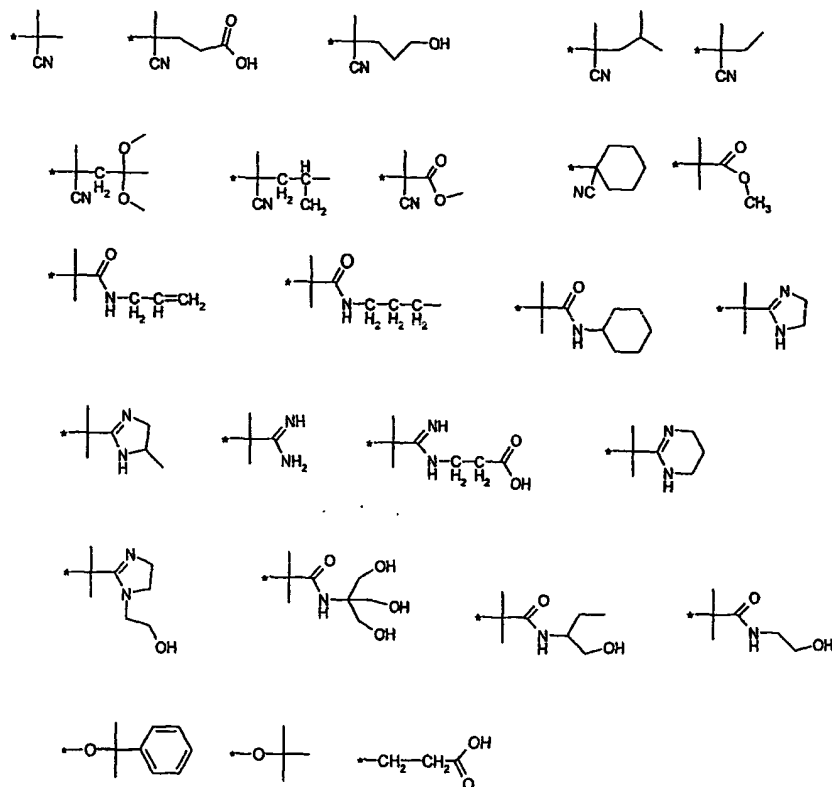
R is selected from a group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups;

n = an integer of at least 1

x = an integer greater than 1.

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8. A method as claimed in any preceding claim wherein the group R', R1, R2, R3 and/or R is selected from the group consisting of:



5

9. A method as claimed in any preceding claim wherein the olefinically unsaturated monomer or comonomers are selected from the group consisting of: methyl methacrylate, ethyl acrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, acrylates and styrenes selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all

isomers), N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-tert-butylmethacrylamide, N-n-butylmethacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers),
 5 diethylaminostyrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), diethylamino alpha-methylstyrene (all isomers), p-vinylbenzenesulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropylmethacrylate,
 10 dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate,
 15 dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, isoprene,
 20 chloroprene, ethylene, propylene, 1,5-hexadienes, 1,4-hexadienes, 1,3-butadienes, and 1,4-pentadienes.

10. A method as claimed in any of claims 1 to 8 wherein the polymerizable monomer or comonomers selected from the group consisting of: vinyl acetate, N-vinyl formamide,
 25 N-alkylvinylamine, allylamine, N-alkylallylamine, diallylamine, N-alkyldiallylamine, alkylidenimine, acrylic acids, alkylacrylates, acrylamides, methacrylic acids, alkylmethacrylates, methacrylamides, N-alkylacrylamides, N-alkylmethacrylamides, styrene, vinyl naphthalene, vinyl pyridine, ethylvinylbenzene, aminostyrene, vinylbiphenyl, vinylanisole, vinylimidazolyl, vinylpyridinyl,
 30 dimethylaminomethylstyrene, trimethylammonium ethyl methacrylate, trimethylammonium ethyl acrylate, dimethylamino propylacrylamide, trimethylammonium ethylacrylate, trimethylammonium ethyl methacrylate,

trimethylammonium propyl acrylamide, dodecyl acrylate, octadecyl acrylate, and octadecyl methacrylate.

11. A method as claimed in any of claims 1 to 8 wherein the polymerizable monomer or comonomers are selected from a group consisting of alkylacrylamides, methacrylamides, acrylamides, styrenes allylamines, allylammonium diallylamines, diallylammoniums, alkylmethacrylates, alkylacrylates, methacrylates, acrylates, n-vinyl formamide, vinyl ethers, vinyl sulfonate, acrylic acid, sulfobetaines, carboxybetaines, phosphobetaines, and maleic anhydride.
12. A method as claimed in claims 1 to 8 wherein the polymerizable monomer or comonomers are selected from the group consisting of: alkylmethacrylates, alkylacrylates, methacrylates, acrylates, alkylacrylamides, methacrylamides, acrylamides, and styrenes.
13. A method as claimed in any preceding claim wherein the first initiator is selected from the group consisting of: 2,2'-azobis(isobutyronitrile), 4,4'-azobis(4-cyanopentanoic acid), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis(2-methylpropane), 2,2'-Azobis[2-(5-methyl-2-imidazolin-2-yl)propane]dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] disulfate dehydrate, 2,2'-Azobis(2-methylpropionamide)dihydrochloride, 2,2'-Azobis[N-(2-carboxyethyl)-2-methylpropionamide]tetrahydrate, 2,2'-Azobis[2-(3,4,5,6-tetrahydropyrimidin-2-yl)propane] dihydrochloride, 2,2'-Azobis{2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propane}dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane], 2,2'-Azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, 2,2'-Azobis{2-methyl-N-[2-(1-hydroxybutyl)]propionamide}, 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile), 2,2'-Azobis(2,4-dimethyl valeronitrile), Dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-Azobis(2-methylbutyronitrile), 1,1'-Azobis(cyclohexane-1-carbonitrile), 2,2'-Azobis[N-(2-propenyl)-2-methylpropionamide], 1-[(cyano-1-methylethyl)azo] formamide, 2,2'-Azobis(N-butyl-2-methylpropionamide), 2,2'-Azobis(N-cyclohexyl-2-methylpropionamide), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butylperoxy

isobutyrate, t-amyl peroxy-pivalate, t-butyl peroxy-pivalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl, hyponitrite, and dicumyl hyponitrite.

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14. Method according to any preceding claim, wherein the second initiator is selected from the group consisting of : 2,2'-azobis(isobutyronitrile), 4,4'-azobis(4-cyanopentanoic acid, 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis (2-methylpropane), 2,2'-Azobis[2-(5-methyl-2-imidazolin-2-yl)propane]dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] disulfate dehydrate, 2,2'-Azobis(2-methylpropionamide)dihydrochloride, 2,2'-Azobis[N-(2-carboxyethyl)-2-methylpropionamide]tetrahydrate, 2,2'-Azobis[2-(3,4,5,6-tetrahydropyrimidin-2-yl)propane] dihydrochloride, 2,2'-Azobis{2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propane} dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane], 2,2'-Azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide, 2,2'-Azobis{2-methyl-N-[2-(1-hydroxybutyl)]propionamide}, 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile), 2,2'-Azobis(2,4-dimethyl valeronitrile), Dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-Azobis(2-methylbutyronitrile), 1,1'-Azobis(cyclohexane-1-carbonitrile), 2,2'-Azobis[N-(2-propenyl)-2-methylpropionamide], 1-[(cyano-1-methylethyl)azo] formamide, 2,2'-Azobis(N-butyl-2-methylpropionamide), 2,2'-Azobis(N-cyclohexyl-2-methylpropionamide), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxy-pivalate, t-butyl peroxy-pivalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl, hyponitrite, and dicumyl hyponitrite.

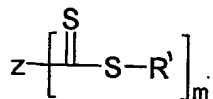
15. A method as claimed in any preceding claim when the reaction is carried out in a solvent selected from the group consisting of: water, alcohol, tetrahydrofuran dimethyl sulfoxide, dimethylformamide, acetone, acetonitrile, benzene, toluene and mixtures thereof.

16. A method as claimed in any preceding claim wherein a reaction is carried out at a temperature in the range of -20 to +200°C.
- 5 17. A method as claimed in claim 16 wherein the reaction is carried out at a temperature in the range of 20 to 150°C.
18. A method as claimed in claim 17 wherein the reaction is carried out at a temperature in the range of 20 to 120°C.
- 10 19. A method as claimed in claim 18 wherein the reaction is carried out at a temperature in the range of 60 to 90°C.
20. A method according to any preceding claim comprising the step of reacting a
15 first supported thiocarbonyl thio compound of Formula (3) or Formula (4) with the olefinically unsaturated monomer (Q) and the first source of free radical to form a polymer of Formula (6) or Formula (7) in the presence of a second non-supported thiocarbonyl compound, and the first and second thiocarbonyl having identical groups R'.
- 20 21. A method of carrying out a reversible-addition-fragmentation chain transfer (RAFT) polymerisation comprising the steps of reacting olefinically unsaturated monomers with a first supported chain transfer agent, in the presence of a second unsupported chain transfer agent, in the presence of a free radical source, to form a
25 polymer.
22. A method according to claim 20 or claim 21 comprising a greater concentration of supported compound than non-supported compound.
- 30 23. A method of producing a block copolymer comprising reacting a first unsaturated monomer by a method according to any one of claims 1 to 20, wherein the thiocarbonyl thio compound of Formula (3) is supported on a solid support, recovering polymer attached to the solid support, and then reacting the recovered polymer by the method of

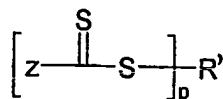
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any one of claims 1 to 20 with a second unsaturated monomer to form a block copolymer.

24. A compound for use in a method according to any preceding claim comprising the formula:



Formula (3)



Formula (4)

10 where:

Z is a solid support or a solid support attached via a linker to the thiocarbonyl thio moiety,

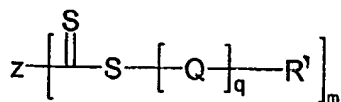
m = an integer of at least 1,

p = an integer of at least 1,

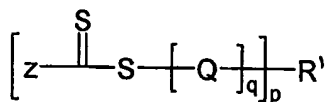
- 15 R' is selected from the group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups.

20

25. A polymer having the formula:



(6)



25

(7)

where:

Z is a solid support or a solid support attached via a linker to the thiocarboxyl thio moiety,

5 m = an integer of at least 1,

p = an integer of at least 1,

q = an integer of at least 2,

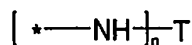
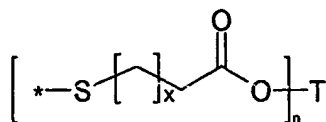
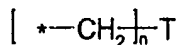
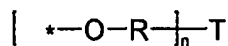
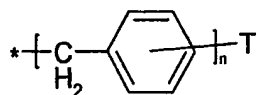
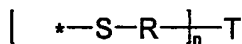
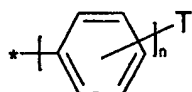
R' is selected from the group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring,
 10 optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups,

Q is at least one olefinically unsaturated monomer, optionally two or more different olefinically unsaturated monomers.

15

26. A compound or polymer according to claim 24 or claim 25,

wherein Z is selected from:



wherein T is a solid support selected from an organic compound, an inorganic compound or magnetised beads,

5 R is selected from a group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups,

n = an integer of at least 1.

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27. A polymer obtainable by a method according to any one of claims 1 to 22.